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TITLE: Ultrafine **fiber** entangled sheet and method of producing the same

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REF-CITED:

U.S. PATENT DOCUMENTS

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL		
4145468	March 1979	Mizoguchi et al.	428/299	N/A	N/A
4146663	March 1979	Ikeda et al.	428/299	N/A	N/A
4198461	April 1980	Heller et al.	428/301	N/A	N/A

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ABSTRACT:

An entangled non-woven fabric having a **fiber** structure which comprises a portion (A) in which ultrafine **fiber** bundles consisting of ultrafine **fibers** of a size of not greater than about 0.5 denier are entangled with one another and a portion (B) in which ultrafine **fibers** to fine bundles of ultrafine **fibers** branch from the ultrafine **fiber** bundles and are entangled with one another, and in which portions (A) and (B) are nonuniformly distributed in the direction of fabric thickness. The product of this invention has high flexibility as well as good shape retention.

The invention also relates to a grained sheet having on at least one of its surfaces a grain formed by a **fiber** structure composed of ultrafine **fibers** to fine bundles of ultrafine **fibers** and having a distance between the **fiber** entangling points of not greater than about 200 microns, and a resin in the gap portions of the **fiber** structure. The grained sheet of the invention has high flexibility resistance, shearing fatigue resistance and scratch and scuff resistance.

41 Claims, 4 Drawing figures

Exemplary Claim Number: 1

Number of Drawing Sheets: 3

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Abstract Text - ABTX (1):

An entangled non-woven fabric having a **fiber** structure which comprises a portion (A) in which ultrafine **fiber** bundles consisting of ultrafine **fibers** of a size of not greater than about 0.5 denier are entangled with one another and a portion (B) in which ultrafine **fibers** to fine bundles of ultrafine **fibers** branch from the ultrafine **fiber** bundles and are entangled with one another, and in which portions (A) and (B) are nonuniformly distributed in the direction of fabric thickness. The product of this invention has high flexibility as well as good shape retention.

Abstract Text - ABTX (2):

The invention also relates to a grained sheet having on at least one of its surfaces a grain formed by a **fiber** structure composed of ultrafine **fibers** to fine bundles of ultrafine **fibers** and having a distance between the **fiber** entangling points of not greater than about 200 microns, and a resin in the gap portions of the **fiber** structure. The grained sheet of the invention has high flexibility resistance, shearing fatigue resistance and scratch and scuff resistance.

TITLE - TI (1):

Ultrafine **fiber** entangled sheet and method of producing the same

Brief Summary Text - BSTX (3):

This invention relates to a novel ultrafine **fiber** entangled sheet and a method for the production thereof. More particularly, the present invention

relates to a novel entangled non-woven fabric having a **fiber** structure which includes a layer comprised of ultrafine **fiber** bundles that are entangled with one another and a layer comprised of ultrafine **fibers** to fine bundles of ultrafine **fibers** wherein both layers are nonuniformly distributed in the direction of fabric thickness, and to a method of producing the entangled non-woven fabric. Further, the present invention relates to a novel grained sheet having a grain composed of densely entangled ultrafine **fibers** to fine bundles of the ultrafine **fibers** and resin and to a method of producing the novel grained sheet.

Brief Summary Text - BSTX (5):
Typical examples of conventional non-woven fabrics include (1) non-woven fabric which is produced by webbing conventional staple **fibers** into a random web and then needle-punching the web, and (2) non-woven fabric as disclosed in Japanese Patent Publication No. 24699/1969 which has a **fiber** structure which consists principally of single **fibers** that are gathered and **bundled, and in which the fiber** bundles are entangled with one another while maintaining the bundle form. However, since fabric (1) has a **fiber** structure which is relatively thick and the **fibers** are individually three-dimensionally entangled with one another, the non-woven fabric has low flexibility and very poor tactile properties. Hence, the commercial value of this non-woven fabric has been considerably limited. Although fabric (2) has higher flexibility than fabric (1), non-woven fabric (2) has extremely low shape retention.

Brief Summary Text - BSTX (9):
(2) Ultrafine **fibers** are arranged along the surface and combined with a porous material to form the grain. (Japanese Patent Publication No. 40921/1974).

Brief Summary Text - BSTX (10):
(3) A surface fluff **fiber** and resin are combined to form the grain.

Brief Summary Text - BSTX (11):
(4) The surface **fibers** are melted or dissolved so as to locally bond the **fibers** and form the grain.

Brief Summary Text - BSTX (12):
However, method (1) has drawbacks in that the flexibility is reduced and the grain luster of the product is diminished by addition of the filters. Since the product obtained by method (2) has a grain **fiber** structure in which the ultrafine **fibers** are arranged along the surface in bundle form, the surface fluffs and peeling develops along the surface of the arrangement of the **fiber**

bundles to cause "loose grain" if the sheet or leather is strongly crumpled or shearing stress is repeatedly applied to the sheet. Where the crumpling, or repeated shearing stress continues, cracks eventually occur on the surface. Moreover, fine unevenness occurs on the surface along the bundles of the ultrafine **fibers** and degrades the surface appearance. The products obtained by methods (3) or (4) have drawbacks in that the surface cracks relatively easily, severely degrading the appearance, when the sheet is repeatedly bent or shearing stress is repeatedly applied to the sheet.

Brief Summary Text - BSTX (19):
First, the present invention provides an entangled non-woven fabric which includes a portion (A) comprised of ultrafine **fiber** bundles of ultrafine **fibers** having a size not greater than about 0.5 denier which bundles are entangled with one another, and a portion (B) comprised of ultrafine **fibers** to fine bundles of ultrafine **fibers** branching from the ultrafine **fiber** bundles which ultrafine **fibers** and fine bundles of ultrafine **fibers** are entangled with one another, and in which both portions (A) and (B) are nonuniformly distributed in the direction of fabric thickness. The present invention also provides a method of producing such an entangled non-woven fabric.

Brief Summary Text - BSTX (20):
Second, the present invention provides a grained sheet having on at least one of its surface a grain formed by a composite structure comprised of a **fiber** structure composed of ultrafine **fibers** to fine bundles of ultrafine **fibers** and having a distance between the **fiber** entangling points not greater than about 200 microns, and a resin in the gap portions of the **fiber** structure. The present invention also provides a method of producing such a grained sheet.

Drawing Description Text - DRTX (4):
FIG. 3 is a schematic view of entangled constituent **fibers** of the grain on the surface side of the grained sheet of the present invention; and

Drawing Description Text - DRTX (5):
FIGS. 4(a) to 4(o) are schematic sectional views showing typical examples of **fibers** which may be used to form the ultrafine **fibers** employed in the present invention.

Detailed Description Text - DETX (2):
The term "ultrafine **fiber** bundle" as used herein denotes **fiber** bundle in which a plurality of **fibers** in staple or filament form are arranged in parallel with one another. The **fibers** may be all of the same type or a combination of **fiber** types may be used. The entangled non-woven fabric in accordance with the

present invention has a **fiber** structure including a portion (A) in which the ultrafine **fibers** are three-dimensionally entangled with one another in bundle form without substantially collapsing the state of arrangement described above and a portion (B) in which ultrafine **fibers** to fine bundles of ultrafine **fibers** branched from the ultrafine **fiber** bundles of portion (A), the fine bundles of ultrafine **fibers** being thinner than the **fiber** bundles of portion (A), are densely entangled with one another or with the unbranched **fiber** bundles extending from the portion (A), and portion (A) and (B) are nonuniformly distributed in the direction of fabric thickness. The **fiber** that forms the entangled non-woven fabric of the present invention has a **fiber** structure such that one ultrafine **fiber** is one of **fibers** constituting a bundle at some portions of the bundle and branches from the bundle at the other portions of the bundle. Therefore, the ultrafine **fiber** bundle and the **fibers** branched from the bundle are not independent.

Detailed Description Text - DETX (3):

An entangled non-woven fabric whose entire portion consists of portion (A) is formed by means of the entanglement of the **fiber** bundles with one another. Accordingly, since the entanglement is not dense and can be easily loosened, the non-woven fabric is extremely likely to undergo deformation and it is difficult for the non-woven fabric to retain its shape particularly in a wet or hydrous state.

Detailed Description Text - DETX (4):

In an entangled non-woven fabric whose entire portion consists of portion (B), on the other hand, the entanglement of the **fibers** of the non-woven fabric as a whole is very dense and mutual restriction of **fiber** movement occurs so that the non-woven fabric has insufficient flexibility.

Detailed Description Text - DETX (5):

The objects of the present invention can be accomplished only when portions (A) and (B) are nonuniformly distributed in the direction of the thickness of the fabric. It is particularly preferred that portion (B) be nonuniformly distributed along the surface portion. Such a non-woven fabric has less fraying of the surface **fibers** and resists pilling. If the non-woven fabric has a **fiber** structure in which the ultrafine **fibers** constituting portions (A) and (B) are substantially continuous and the degree of branching of the **fibers** in the proximity of the boundary between the portions changes continuously, the non-woven fabric has integral hand characteristics such as flexibility and suppleness and portions (A) and (B) do not peel from one another.

Detailed Description Text - DETX (6):

FIG. 1 illustrates an embodiment of the entangled non-woven fabric in accordance with the present invention. In FIG. 1, A denotes the portion in which ultrafine **fiber** bundles are entangled with one another and B denotes the portion in which ultrafine **fibers** and fine bundles of ultrafine **fibers** branch from the ultrafine **fiber** bundles and are entangled with one another. FIGS. 2(a) to 2(g) illustrate embodiments in which portions A and B are nonuniformly distributed in the direction of thickness.

Detailed Description Text - DETX (7):
The grained sheet in accordance with the present invention is a composite structure whose grain is comprised of ultrafine **fibers** to fine bundles of ultrafine **fibers** and of a resin present in the gap portions of the **fibers** and the fine bundles. The fundamental structure is one in which ultrafine **fibers** and fine bundles of ultrafine **fibers** are densely entangled with one another. Only this combination can provide a grained sheet having good hand characteristics such as flexibility and suppleness, smooth surface, high flexibility resistance, shearing fatigue resistance and scratch and scuff resistance.

Detailed Description Text - DETX (8):
It is required that the **fiber** structure in the grain of the grained sheet of the present invention be such that the ultrafine **fibers** and the fine bundles of the ultrafine **fibers** densely entangled with one another. In other words, it is necessary that the entanglement density of the **fibers** be high. One of the methods of measuring the entanglement density of the **fibers** is to measure the distance between the **fiber** entanglement points. A short distance between points of entanglement evidences a high density of entanglement.

Detailed Description Text - DETX (9):
The distance between the **fiber** entanglement points is measured in the following manner. FIG. 3 is an enlarged schematic view of the constituent **fibers** in the grain when viewed from the surface side. It will be assumed that the constituent **fibers** are f.sub.1, f.sub.2, f.sub.3, . . . , the point at which two arbitrary **fibers** f.sub.1 and f.sub.2 among them are entangled with each other is a.sub.1 and the point at which the upper **fiber** f.sub.2 is entangled with another **fiber with the fiber** f.sub.2 being the lower **fiber** is a.sub.2 (the entanglement point between f.sub.2 and f.sub.3). Similarly, the entanglement points a.sub.3, a.sub.4, a.sub.5, . . . are determined. The linear distances a.sub.1 a.sub.2, a.sub.2 a.sub.3, a.sub.3 a.sub.4, a.sub.4 a.sub.5, a.sub.5 a.sub.6, a.sub.6 a.sub.7, a.sub.7 a.sub.3, a.sub.3 a.sub.8, a.sub.8 a.sub.7, a.sub.7 a.sub.9, a.sub.9 a.sub.6, . . . measured along the surface are the distance between the **fiber** entangling points.

Detailed Description Text - DETX (10):
In the present invention, the **fibers** of the grain must have an entanglement density of not greater than about 200 microns as measured by this method. In **fiber** structures where the entanglement density is greater than about 200 microns, such as in those **fiber** structures in which the entanglement of the **fibers** is effected only by needle punching, in which ultrafine **fibers** or bundles are merely arranged along the surface or, in which thickly raised ultrafine **fibers** or bundles are laid down on the surface of a substrate to form the grain, little or no entanglement of the **fibers** occurs. When friction, crumpling and shearing stress are repeatedly applied to such fabrics the surface is likely to fluff unsightly or to develop cracks. To eliminate these problems, the distance between the **fiber** entangling points must be not greater than 200 microns. More favorable results are obtainable when the distance is not greater than about 100 microns.

Detailed Description Text - DETX (11):
There are no specific requirements for the structure of the layer below the grain of the grained sheet in accordance with the present invention and this layer may be suitably constructed in accordance with the intended application. However, the lower layer preferably has the following structure. The lower layer of the grained sheet preferably has a **fiber** structure in which ultrafine **fiber** bundles are entangled with one another, ultrafine **fibers** and the fine bundles of ultrafine **fibers** of the grain are formed as the ultrafine **fiber** bundles of the lower layer branch and are densely entangled with one another, the **fibers** in the grain are substantially continuous with the **fibers** in the lower layer and, moreover, the degree of branching of the **fibers** continuously changes at the boundary between both layers. Such a **fiber** structure provides a sheet having integral hand characteristics and prevents peeling of the grain from the lower layer. In this instance, it is not necessary that the size of the fine bundles of ultrafine **fibers** of the grain be all the same. If the size of the bundles of the ultrafine **fibers** of the grain is less than that of the ultrafine **fibers** of the lower layer, or if the number of **fibers** contained in one bundle of the grain is smaller than that of the lower layer, unevenness does not easily occur on the surface of the sheet.

Detailed Description Text - DETX (13):
In contrast, the grained sheet of the present invention, having a **fiber** structure in which the ultrafine **fibers** and the fine bundles of the ultrafine **fibers** of the grain are densely entangled with one another, is not seriously deformed under application of in-use tensional forces and has good shape retention even when resin is not applied to the lower layer. This is also one

of the most characterizing features of the grained sheet of the present invention. Needless to say, resin such as polyurethane elastomer may be applied to the lower layer and deposition quantity of the resin varies depending upon the application of the sheet. For example, when the sheet is to be used for apparel, the resin deposition quantity is preferably 0 to 80 parts by weight based on the weight of the **fibers**.

Detailed Description Text - DETX (14):

Resins which may be used ~~for the~~ grained sheet are synthetic or natural polymer resins such as **polyamide**, polyester, polyvinyl chloride, polyacrylate copolymers, polyurethane, ~~neoprene~~, styrene butadiene copolymers, acrylonitrile/butadiene copolymers, polyamino acids, polyamino acid/polyurethane copolymers, silicone resins and the like. Mixtures of two or more resins may also be used. If necessary, additives such as plasticizers, fillers, stabilizers, pigments, dyes, cross-linking agents, and the like may be further added. Polyurethane elastomeric resin, either alone or mixed with other resins or additives, is preferably used because it provides a grain having particularly good hand characteristics such as flexibility and suppleness, good touch and high flexibility resistance.

Detailed Description Text - DETX (15):

The deposition structure of the resin in the grain is dependent on the intended application. Where flexibility and soft touch are required such as in apparel, preferred structures are those in which the resin is applied in a progressively increasing amount towards the surface of the grain. The resin deposition quantity is the greatest in an extremely thin layer on the outermost surface of the grain with little or no resin at other portions. The resin at the surface portion is non-porous, whereas the portion below the surface portion is porous. Where high scratch and scuff resistance are particularly required, a preferred **fiber** structure is one where the resin is packed substantially fully into the gap portions of the grain without leaving any gaps intact. The grained sheet in accordance with the present invention includes, of course, one in which the outermost surface of the grain consists of a thin resin layer of up to about 30 microns of a resin such as a polyurethane elastomer which is integrated with the other portions.

Detailed Description Text - DETX (16):

As the ultrafine **fibers** to be used in the present invention, there may be mentioned those which are produced by various direct methods, such as super-draw spinning, jet spinning using a gas stream, and so forth. In accordance with these methods, however, spinning would become unstable and difficult if the **fiber** size becomes too fine. For these reasons, it is

preferred to employ the following types of **fibers** which are formable into ultrafine **fiber** and to modify them into ultrafine **fibers** at a suitable stage of the production process. Examples of such ultrafine **fiber** formable **fibers** include those having a chrysanthemum-like cross-section in which one component is radially interposed between other components, multi-layered **bicomponent** type **fibers,** multi-layered **bicomponent** type **fibers** having a doughnut-like cross-section, mixed spun **fibers** obtained by mixing and spinning at least two components, islands-in-a-sea type **fibers which have a fiber** structure in which a plurality of ultrafine **fibers** that are continuous in the direction of the **fiber** axis are arranged and aggregated and are bounded together by other components to form a **fiber,** specific islands-in-a-sea **fibers which have a fiber** structure in which a plurality of extra-ultrafine **fibers** are arranged and aggregated and are bonded together by other components to form an ultrafine **fiber** and a plurality of these ultrafine **fibers** are arranged and aggregated and are bonded together by other components to form a **fiber,** and so forth. Two or more of these **fibers** may be mixed or combined.

Detailed Description Text - DETX (17):

It is preferable that ultrafine **fiber** formable **fibers having a fiber** structure in which a plurality of cores are at least partially bonded by other binding components, because they provide relatively readily ultrafine **fibers** by applying physical or chemical action to them or by removing only the binding components.

Detailed Description Text - DETX (18):

FIGS. 4(a) to 4(o) show examples of the ultrafine **fiber** formable **fibers** which may be used to obtain the ultrafine **fibers**. In FIGS. 4(a) to 4(o), reference numerals 1 and 1' represent ultrafine **fibers** and reference numerals 2 and 2' represent binding components. The ultrafine **fibers** may be composite **fibers** consisting of similar polymer materials in kind or different polymer materials in kind. Other types of **fibers** which may be used include **crimped fibers,** modified cross-section **fibers,** hollow **fibers,** multi-hollow **fibers** and the like. Further, ultrafine **fibers** of different kinds may be mixed.

Detailed Description Text - DETX (19):

The size of the ultrafine **fibers** in the entangled non-woven fabric in accordance with the present invention must not be greater than about 0.5 deniers. If the denier is greater than 0.5, the stiffness of the **fibers** is so great that the resulting non-woven fabric has low flexibility and it is difficult to densely entangle the **fibers**.

Detailed Description Text - DETX (20):

The ultrafine **fibers** in the grain of the grained sheet of the present invention are preferably not greater than about 0.2 denier. If the **fibers** are greater than 0.2 deniers, the **fiber** stiffness is so great that the grain looses flexibility, the surface develops unsightly creases and cracks, surface unevenness is likely to occur upon crumpling of the sheet and it is difficult to form a dense and flexible grain. Only with ultrafine **fibers** having a size not greater than about 0.2 denier, more preferably, not greater than about 0.05 denier, can a leather-like sheet be obtained which has a grain **fiber** structure in which the **fibers** are densely entangled with one another, which has excellent smoothness, which is soft and which is resistance to development of cracks. Multiple-component ultrafine **fiber** formable **fibers, which provide fiber** bundles principally comprised of ultrafine **fibers** having a denier not greater than about 0.2, preferably not greater than about 0.05 denier, and in which at least one component may be dissolved and removed, and preferably employed. Such **fibers** can provide a grained sheet having particularly excellent hand characteristics, such as flexibility and suppleness, and a smooth surface. Those **fibers** which have a specific **fiber** structure in which a plurality of extra-ultrafine **fibers** are arranged and aggregated and are bonded together by other components to form one ultrafine **fiber** (primary bundle) and a plurality of these ultrafine **fibers** are arranged and aggregated and are bonded together by other components to form one **fiber** (secondary bundle) can be fibrillated extremely finely and entangled densely when they are subjected to high speed fluid jet streams. Hence, such **fibers** provide a grained sheet having extremely soft and excellent touch.

Detailed Description Text - DETX (21):

The ultrafine **fibers** of the present invention consist of polymer material having **fiber** formability. Examples of the polymer material include **polyamides,** such as nylon 6, nylon 66, nylon 12, copolymerized nylon, and the like; polyesters, such as polyethylene terephthalate, polybutylene terephthalate, copolymerized polyethylene terephthalate, copolymerized polybutylene terephthalate, and the like; polyolefins, such as polyethylene, polypropylene, and the like; polyurethane; polyacrylonitrile; vinyl polymers; and so forth. Examples of the binding component of the ultrafine **fiber** formable **fibers,** or the component which is to be dissolved for removal, include polystyrene, polyethylene, polypropylene, **polyamide,** polyurethane, copolymerized polyethylene terephthalate that can be easily dissolved in an alkaline solution, polyvinyl alcohol, copolymerized polyvinyl alcohol, styrene/acrylonitrile copolymers, copolymers of styrene with higher alcohol esters of acrylic acid and/or with higher alcohol esters of methacrylic acid, and the like.

Detailed Description Text - DETX (22):

From the aspect of **fiber** spinnability, as well as dissolvability for removal of the binding component, however, polystyrene, styrene/acrylonitrile copolymers, and copolymers of styrene with higher alcohol esters of acrylic acid and/or with higher alcohol esters of methacrylic acid and preferably used. The copolymers of styrene with higher alcohol esters of acrylic acid and/or with higher alcohol esters of methacrylic acid are further preferably used because during drawing they provide a higher draw ratio and **fibers** having higher strength.

Detailed Description Text - DETX (23):

In order to to easily fibrillate the ultrafine **fiber** formable **fibers** it is preferred to mix some amount of heterogeneous substance to the binding component before spinning. Such heterogeneous substance makes easy to break or remove the binding component by treating with high speed fluid jet streams. Thus the ultrafine **fiber** formable **fibers** are fibrillated into ultrafine **fibers** or fine bundles of ultrafine **fibers** and densely entangled. Examples of the heterogeneous substances include polyalkyleneetherglycols, such as polyethyleneetherglycol, polypropyleneetherglycol, polytetramethyleneetherglycol and the like; substituted polyalkyleneetherglycols such as methoxypolyethyleneetherglycol and the like; block or random copolymers such as block copolymer of ethyleneoxide and propyleneoxide, random copolymer of ethyleneoxide and propyleneoxide, and the like; alkyleneoxide additives of alcohols, acids or esters, such as ethyleneoxide additive of nonylphenol and the like; block copolymers of polyalkyleneethervlycols and other polymers, such as block polyetherester of polyethyleneetherglycol and various polyesters, block polyetheramide of polyethyleneetherglycol and various **polyamides**; polymers mentioned above as the binding component in combination with different polymer as the binding component; fine particles of inorganic compounds such as calcium carbonate, talc, silica, colloidal silica, clay, titanium oxide, carbon black and the like; mixtures thereof and so forth.

Detailed Description Text - DETX (26):

Preferred amount of heterogeneous substance varies according to intended use. In case of polyalkyleneetherglycol, 0.5 to 30 wt%, based on the total amount of binding component, is preferable. 2 to 20 wt% is most preferable. If the amount is under 0.5 wt%, the fibrillation effect is inferior, and if the amount is over 30 wt%, **fiber** spinnability becomes worse.

Detailed Description Text - DETX (27):

There is no limitation, in particular, to the size of the ultrafine **fiber**

formable **fibèrs** but the preferred size range is from about 0.5 to 10 denier in view of spinning stability and ease of sheet formation.

Detailed Description Text - DETX (28):

The method of producing the entangled non-woven fabric in accordance with the present invention comprises, for example, forming a web by use of **fiber** bundles which are obtained by bundling ultrafine **fibers** obtained in the manner described above and temporarily treating them with a binding component to retain the **fibers** in bundle form, or by use of filaments or staple **fibers** of ultrafine **fiber** formable **fibers,** then optionally needle-punching the resulting web to form an entangled structure and thereafter removing the binding component using a solvent which can dissolve only the binding component. Thereafter, the resulting entangled structure is treated with high speed fluid jet streams so as to branch the ultrafine **fibers** and the fine bundles of ultrafine **fibers** from the ultrafine **fiber** bundles and to simultaneously entangle the branching ultrafine **fibers** and the fine bundles of ultrafine **fibers**. A step of applying a paste, such as polyvinyl alcohol, to temporarily fix the non-woven fabric as a whole after the entangled structure is formed by needle-punching, and removing the paste after dissolution and removal of the binding component or simultaneously effecting the high speed fluid jet streams treatment with the removal of the paste, so as to prevent the collapse of the shape of the non-woven fabric at the time of dissolution and removal of the binding component may optionally be used in the process. The treatment with the high speed fluid jet streams may be effected before the binding component is removed.

Detailed Description Text - DETX (29):

In some cases, branching of the **fibers** by treatment with the high speed fluid jet streams is not sufficiently effected because the ultrafine **fibers** are bonded together by the binding component. In such cases, branching can be accomplished extremely effectively by the following method. A polymer, such as polyethylene glycol, is added to the binding component for the ultrafine **fibers** or, alternatively a substance that can degrade or plasticize the binding component is applied to the **fiber** sheet before the treatment with the high speed fluid jet streams.

Detailed Description Text - DETX (31):

In order to obtain the structure of the entangled non-woven fabric of the present invention, the apparent density of the non-woven fabric before the treatment with the high speed fluid jet streams is preferably from about 0.1 to 0.6 g/cm.sup.3. If the apparent density is below about 0.1 g/cm.sup.3, the **fibers** move easily and those pushed by the fluid jet streams penetrate through

the non-woven fabric and intrude into the metal net on which the non-woven fabric is placed, so that severe unevenness appears on the surface of the non-woven fabric. If the apparent density is above about 0.6 g/cm.sup.3, the fluid jet streams are reflected on the surface of the non-woven fabric and entanglement is not sufficiently accomplished.

Detailed Description Text - DETX (33):
There is no limitation, in particular, to the shape of the jet nozzle main body, but a transverse nozzle having a number of orifices having a diameter of about 0.01 to 0.5 mm that are aligned with narrow gaps between, in a line or in a plurality of lines can be conveniently used to obtain a **fiber** sheet having less surface unevenness and uniform properties.

Detailed Description Text - DETX (34):
The gap between the adjacent orifices is preferably from about 0.2 to 5 mm in terms of the distance between the centers of these orifices. If the gap is smaller than about 0.2 mm, machining of the orifices becomes difficult and the high speed fluid jet streams are likely to come into contact with streams from adjacent orifices. If the gap is greater than about 5 mm, the surface treatment of the **fiber** sheet must be carried out many times.

Detailed Description Text - DETX (35):
The pressure applied to the fluid varies with the properties of the non-woven fabric and can be freely selected within the range of about 5 to 300 kg/cm.sup.2. The high speed fluid jet streams may contact the **fiber** sheet several times, the pressure for each jet may be varied or the nozzle or non-woven fabric may be oscillated during jetting to optimize fabric properties.

Detailed Description Text - DETX (36):
The binding component used for bundling and temporarily bonding the ultrafine **fibers** are preferably those which can be easily removed by water for industrial economy. Examples of such components are starch, polyvinyl alcohol, methylcellulose, carboxymethylcellulose and the like. Synthetic and natural pastes and adhesives that can be dissolved by solvents can also be used. Examples of such pastes and adhesives are vinyl type latex, polybutadiene type adhesives, polyurethane type adhesives, polyester type adhesives, **polyamide** type adhesives, and so forth.

Detailed Description Text - DETX (37):
In the production of the entangled non-woven fabric in accordance with the present invention, it is not necessary to use wholly ultrafine **fibers** and a

combined use of other **fibers** may be permitted in so far as it does not diverge from the object of the present invention. It is also possible to incorporate resin binder as well.

Detailed Description Text - DETX (38):

The grained sheet in accordance with the present invention may be produced by the following method. The ultrafine **fiber** formable **fibers** are first produced by use of a spinning machine such as one disclosed in Japanese Patent Publication No. 18369/1969, for example, and are then converted into staple **fiber,** and the resulting staple **fibers** are passed through a card and a cross lapper to form a web. The web is needle-punched to entangle the ultrafine **fiber** formable **fibers** and to form a **fiber** sheet. Alternatively, after the ultrafine **fiber** formable **fibers** are spun, they are subsequently stretched and are randomly placed on a metal net. The resulting web is needle-punched in the same way as above to obtain the **fiber** sheet. Still alternatively, the ultrafine **fiber** formable **fibers** are placed on a non-woven fabric, woven fabric or knitted fabric consisting of ordinary **fibers** or another kind of ultrafine **fiber** formable **fibers** and are inseparably entangled to form a **fiber** sheet. The **fiber** sheet thus obtained is treated with a high speed fluid jet streams to branch the ultrafine **fiber** formable **fibers** into ultrafine **fibers** to fine bundles of ultrafine **fibers** and to simultaneously entangle the **fibers** and their bundles. The treating method used for the production of the entangled non-woven fabric of the present invention described above can also be used for this high speed fluid jet stream treatment. The non-woven fabric of the present invention described hereinabove can also be preferably used for producing the grained sheet of the present invention.

Detailed Description Text - DETX (39):

If the ultrafine **fiber** formable **fibers** used are of the type which can be modified to ultrafine **fiber** bundles when part of the components are dissolved and removed, the dissolving and removing step is thereafter applied depending on the intended application. If necessary, the sheet is wet-coagulated of dry-coagulated by impregnating the sheet with a solution or dispersion of a polyurethane elastomer or the like. In this instance, part of the **fiber** components may be dissolved and removed before the high speed fluid jet stream treatment. Since the ultrafine **fiber** formable **fibers** of the sheet are modified into bundles of ultrafine **fibers** as part of the components are dissolved and removed, the **fibers** can be highly branched and entangled easily by a low fluid pressure. The high speed fluid jet stream treatment may be effected both before and after the dissolving and removing treatment of the component.

Detailed Description Text - DETX (40):

It is further possible to interpose the step of applying the resin between the high speed fluid jet streams treatment and the dissolving and removing step of the component. In this case, it is necessary that the resin should not be dissolved by the solvent used for dissolving and removing the component. Since the component is thus removed, the gaps are defined between the ultrafine **fiber** bundles and the resin of the resulting **fiber** sheet and promote freedom of mutual movement of the **fibers**. Hence, this is a preferred method for providing the resulting sheet with excellent hand characteristics, such as flexibility and suppleness.

Detailed Description Text - DETX (41):

On the other hand, application of the high speed fluid jet stream treatment after the application of the resin is not preferable because, if the deposition quantity of the resin is too great, the **fibers** are restricted by the resin and consequently, branching and entanglement of the **fibers** and their bundles can not readily be effected. Thereafter, the solution or dispersion of the aforementioned grain resin is applied to the layer of the **fiber** sheet in which ultrafine **fibers** to fine bundles of ultrafine **fibers** are entangled with one another, by suitable methods such as reverse roll coating, gravure coating, knife coating, slit coating, spray coating and the like, is then wet-coagulated or dry-coagulated, is put on the surface of a roller or the surface of the plane sheet and is thereafter pressed and, if necessary, heated so as to integrate the **fibers** with the resin and to simultaneously flatten the surface.

Detailed Description Text - DETX (42):

In this case, it is preferred to make the surface of the **fiber** sheet flat by heat-pressing the **fiber** sheet before the application of the grain resin. The use of an embossing roller or a sheet having a grain pattern is preferred because integration, flattening and application of the grain pattern can be simultaneously conducted. If necessary, depending on the final application, coating with a finishing agent, dyeing, crumpling and the like may be carried out.

Detailed Description Text - DETX (43):

In using the grained sheet of the present invention for apparel, the following method is preferably employed if flexibility and soft touch are particularly necessary. A substance that can degrade or plasticize the binding component of the ultrafine **fiber** formable **fibers** is applied to the **fiber** sheet consisting of such ultrafine **fiber** formable **fibers** and high speed fluid jet stream treatment is then carried out. The resulting **fiber** sheet is heat-pressed so as to make the surface to which the high speed fluid jet stream treatment is applied smooth. Next, this surface is coated with a resin

solution of a polyurethane elastomer or the like and is solidified in such a manner that part of the resin penetrates into the sheet and resin remains as a thin layer on the sheet surface. A grain pattern is then applied using an embossing roller on the sheet surface, if necessary, and after the binding component is dissolved and removed, finishing treatments, such as dyeing, application of softening agents, crumpling and the like are carried out.

Detailed Description Text - DETX (44):
The entangled non-woven fabric in accordance with the present invention has high flexibility, retains its shape and has particularly high shape retention when wet such as when the fabric contains a liquid, such as water. Because of these properties, the non-woven fabric can be suitably used for cloths, towels, various **filters, materials** such as grips, various covers, substrates for synthetic leathers, polishing cloths for furniture, automobiles or glass, polishing pads, cassette tape pads, wiping cloths, and so forth.

Detailed Description Text - DETX (46):
The following examples are intended to further clarify the present invention but are in no way limitative. In the examples which follow, the terms "part or parts" and "%" refer to the "part or parts by weight" and "% by weight" unless otherwise stipulated. The value of the average distance of the **fiber** entangling points is a mean value of 100 measured values.

Detailed Description Text - DETX (48):
Islands-in-a-sea type **fibers** (4.5 denier) consisting of 70 parts nylon 6 as the binding component (see component) and 30 parts polyethylene terephthalate containing 0.1% of titanium oxide as the ultrafine **fiber** component (islands component) were treated with formic acid to continuously dissolve and remove nylon 6. The remaining ultrafine polyethylene terephthalate **fibers** consisted of 36 filaments of about 0.038 denier. The **fibers** were then bonded with each other to form **fiber** bundles by use of a paste consisting of a partial saponified polyvinyl alcohol. A large number of **fiber** bundles were gathered in a tow, were then passed through a stuffer box type crimper to apply crimp of about 12 crimps/inch without heating and were subsequently cut to form 51 mm staple **fibers**. The staple **fibers** were passed through a random webber for random webbing and were needle-punched at a rate of 2,500 needles/cm.sup.2 to provide a non-woven fabric having an apparent density of 0.19 g/cm.sup.3.

Detailed Description Text - DETX (49):
After being pressed by a heated roller to achieve an apparent density of 0.21 g/cm.sup.3, the non-woven fabric was placed on a 100 mesh metal net which was being moved and water pressurized to 70 kg/cm.sup.2 was jetted from a

nozzle having a large number of aligned small apertures and a large number of the columnar streams of the water were jetted to the surface of the non-woven fabric. The treatment was repeated three times for each surface of the non-woven fabric in order to effect dissolution of the paste and, at the same time, branching and entanglement of the **fibers**. The fabric was then dried. The resulting dried entangled non-woven fabric consisted of ultrafine **fibers** branching from the portions of about 1/4 thickness from both surfaces and of bundles of such ultrafine **fibers** and had a densely entangled structure. The entangled non-woven fabric had pleasant touch and was soft and not easily deformed.

Detailed Description Text - DETX (50):
For comparative purpose, the non-woven fabric having an apparent density of 0.19 g/cm.sup.3, which was obtained by only needle punching, was dipped into hot water, whereupon the paste was dissolved and along therewith, the non-woven fabric became easily deformable and difficult to handle. Accordingly, the non-woven fabric was placed on a metal net, was left standing still in hot water for a day and night to dissolve and remove the paste, aand was dried. The resulting non-woven fabric had a structure in which the ultrafine **fiber** bundles were loosely entangled with one another in bundle form. Though the non-woven fabric was soft, it was remarkably deformed and its surface was unsightly fluffed when it was slightly pulled or rubbed.

Detailed Description Text - DETX (52):
Filaments, each consisting of 16 multi-hollow type ultrafine **fibers** of nylon 6 of 0.5 denier, were bonded together by a carboxymethylcellulose paste to form a bonded **fiber** bundle. The **crimped fibers** were cut to a length of about 38 mm and were thereafter passed through a card and a cross lapper to obtain a web. The web was needle-punched at a rate of 1500 needles/cm.sup.2 to obtain a non-woven fabric. The resulting non-woven fabric had an apparent density of 0.15 g/cm.sup.3. When it was subjected to treatment with water jet streams under the same conditions as in Example 1, there was obtained an entangled non-woven fabric which was soft and had excellent shape retention. Since this entangled non-woven fabric had extremely high water absorbing characteristics, it was most suitable for various kinds of cloths and towels.

Detailed Description Text - DETX (54):
Islands-in-a-sea type **fibers** of 3.5 denier, having a composition consisting of 30 parts of a vinyl type polymer, obtained by copolymerizing 20 parts of 2-ethylhexylacrylate and 80 parts of styrene, as the binding component (sea component), and 70 parts of polyethylene terephthalate as the ultrafine **fiber** component (islands component), and containing 16 ultrafine **fibers** in one

filament. The **fibers were crimped** and cut to form a web in the same way as in Example 1, followed by needle-punching at a rate of 1500 needle/cm.sup.2 to provide a non-woven fabric(1). Alternatively, 3.5 denier specific islands-in-a-sea type **fibers** having a composition consisting of 45 parts of a mixture of 95 parts of polystyrene and 5 parts of polyethylene glycol, as the binding component (sea component), and 55 parts of polyethylene terephthalate as the extra-ultrafine **fibers** component (islands component) and containing 16 island component groups in one filament with each island component group containing therein a large number of the extra-ultrafine **fibers, were crimped** and were cut to 38 mm staple factors. After the resulting web was passed through a card and a cross lapper, it was sprinkled over the non-woven fabric(1) described above for lamination.

Detailed Description Text - DETX (55):
Subsequently, needle-punching was effected at a rate of 1500 needles/cm.sup.2 from the web side so as to integrate the web with the non-woven fabric(1). The non-woven fabric thus integrated had an apparent density of 0.20 g/cm.sup.3. Water which was pressurized to 100 kg/cm.sup.2 was jetted to the web side of this integrated non-woven fabric while it was being moved, using the same nozzle as that of Example 1 and this treatment was repeated four times. Thus, the **fibers** of the laminated web portion were thinly branched and were densely entangled with one another. Next, the non-woven fabric was dipped into trichloroethylene with dipping and wringing repeated so as to extract and remove substantially completely the binding component. Drying was then effected to evaporate and remove the remaining trichloroethylene. The entangled non-woven fabric thus obtained has extremely soft touch and was shape retentive.

Detailed Description Text - DETX (57):
Staple **fibers,** 51 mm long and 4.0 denier, of islands-in-a-sea type **fibers** disclosed in Japanese Patent Publication No. 37648/1972 were utilized. The **fibers** had a composition consisting of 60 parts of vinyl type polymer obtained by copolymerizing 20 parts of 2-ethylhexylacrylate and 80 parts of styrene, as the binding component (sea component), and 40 parts of nylon 6 as the extra-ultrafine **fiber** component (islands component) and containing 16 island component groups in one filament with each island component group containing therein a large number of the extra-ultrafine **fibers**. The staple **fibers** were passed through a card and a cross lapper to from a web. The web was needle-punched using needles having a hook number of 1, so as to entangle the island-in-a-sea tyep **fibers** and to produce non-woven fabric (A). The non-woven fabric had a weight per unit area of 405 g/m.sup.2 and an apparent density of 0.20 g/cm.sup.3.

Detailed Description Text - DETX (58):

Water which was pressurized to 100 kg/cm.sup.2 was jetted and brought into contact at a high speed with the surface of the non-woven fabric (A) while it was being moved, from a nozzle having a line of apertures having a diameter of 0.1 mm and a distance pitch of 0.6 mm between the centers of the apertures. The non-woven fabric was treated five times and ten times under the same conditions, respectively. Next, the pressure of the water was reduced down to 50 kg/cm.sup.2 and the same treatment was applied once to the non-woven fabrics while oscillating the nozzle, thereby forming non-woven fabrics (B) and (C), respectively. Each of the resulting non-woven fabrics (B) and (C) had a **fiber** structure in which the islands-in-a-sea type **fibers** of the surface layer were branched into ultrafine **fibers** and into fine bundles of ultrafine **fibers** and were densely entangled with one another.

Detailed Description Text - DETX (59):

Each of the non-woven fabrics (A), (B) and (C) was then impregnated with a 7% dimethylformamide solution of polyurethane prepared by chain-extending a prepolymer between a mixed diol consisting of polyethylene adipate diol and polybutylene adipate diol and p,p'-diphenylmethane diisocyanate using ethylene glycol. After the solution adhering to the surface was removed by a scraper, each non-woven fabric was introduced into water and the polyurethane was coagulated. Thereafter, the non-woven fabric was sufficiently washed in hot water at 80.degree. C. to remove the dimethylformamide. After being dried, the non-woven fabric was repeatedly dipped into trichloroethylene and squeezed to extract the vinyl type polymer sea component of the **fibers**. After the resin was extracted and removed substantially completely, the non-woven fabric was dried to evaporate and remove the remaining trichloroethylene.

Detailed Description Text - DETX (60):

The sheets obtained from the non-woven fabrics (B) and (C) were devoid of unevenness and were extremely smooth on the surface to which the water stream treatment was applied but the sheet obtained from non-woven fabric (A) was found to have unevenness extending along the ultrafine **fiber** bundles and had low smoothness. Next, a solution which was prepared by adding a pigment to a 10% solution of polyurethane, which had the same composition as that used for impregnation but had considerably higher hardness, was applied to the surface of each sheet by use of a gravure coater. THe sheet was then dried. The treatment using a gravure coater and the treatment of drying were repeated twice. Thereafter, it was passed through a hot embossing roller for pressing to apply a leather-like grain pattern. Thereafter, the sheet was dyed at a normal pressure using a circulating-liquor dyeing machine and was finished in a

customary manner.

Detailed Description Text - DETX (61):

The grained sheets obtained from the non-woven fabrics (B) and (C) had a smooth surface along the grain pattern, were soft and had integral hand characteristics such as flexibility and suppleness. On the other hand, the sheet obtained from the non-woven fabric (A) exhibited unevenness having vein-like lines extending along the ultrafine **fiber** bundles and dyeing cracks that extended locally along the ultrafine **fiber** bundles. The ultrafine **fibers** appeared at the surface of these cracks.

Detailed Description Text - DETX (62):

The polyurethane and finishing agent applied to these grained sheets were extracted and removed by a solvent and the distance between the **fiber** entangling points were measured. The average distance between the **fiber** entangling points was 361 microns for the sheet prepared from non-woven fabric (A), 193 microns for the sheet prepared from non-woven fabric (B) and 77 microns for the sheet prepared from non-woven fabric (C).

Detailed Description Text - DETX (73):

A non-woven fabric (A) as prepared in Example 4, was dipped into a 5% aqueous solution of polyvinyl alcohol heated to 95.degree. C. in order to effect impregnation of the polyvinyl alcohol and at the same time to cause shrinkage of the non-woven fabric. The non-woven fabric was dried to remove moisture. Thereafter, the non-woven fabric was repeatedly dipped into trichloroethylene and squeezed to extract and remove the vinyl type polymer sea component of the **fiber,** followed by drying of the non-woven fabric. The resulting non-woven fabric was one in which the ultrafine **fibers** were entangled with one another substantially in the form of bundles. Water that was pressurized to 50 kg/cm.sup.2 was jetted at high speed to both surfaces of the non-woven fabric using the same nozzle as used in Example 4, and the treatment was repeated three times for each surface at the same conditions so as to dissolve the polyvinyl alcohol and to simultaneously branch and entangle the **fibers**. The final treatment for each surface was carried out with oscillation of the nozzle. After the polyvinyl alcohol was removed, the non-woven fabric was pressed through a mangle while wet, and was thereafter dried.

Detailed Description Text - DETX (74):

The surface layer of the resulting non-woven fabric had a **fiber** structure in which the original ultrafine **fiber** bundles were branched to a high degree and were densely entangled with one another. Thereafter, one side on the non-woven fabric was buffed using sand paper and a polyurethane solution was applied to

the other surface using a gravure coater with the rest of the subsequent procedures being the same as those in Example 4. There was thus obtained a leather-like sheet.

Detailed Description Text - DETX (75):
Although the shape of the resulting grained sheet was substantially fixed only by the entanglement of the **fibers,** the sheet had excellent shape retention and its **fiber** structure was highly analogous to that of natural leather. The sheet also had high softness and excellent hand characteristics, such as flexibility and suppleness. When bent ends of the fabric were gripped by fingers, the sheet exhibited round touch and shape, and neither cracking nor fluffing occurred when the sheet was strongly rubbed or pulled by hand. When a coat was tailored from this sheet, it was free from paper-like bent creases and had excellent appearance.

Detailed Description Text - DETX (76):
The polyurethane and finishing agent were removed from the grain of this grained sheet using a solvent and the average distance between **fiber** entangling points were measured. It was found to be 13 microns.

Detailed Description Text - DETX (78):
Islands-in-a-sea type **fibers** of 3.8 denier and 51 mm long having a composition consisting of 45 parts of a mixture of 95 parts of polystyrene and 5 parts of polyethylene glycol, as the binding component (sea component), and 55 parts of polyethylene terephthalate as the ultrafine **fibers** component (islands component) and contained 16 ultrafine **fibers** in one filament were used to produce a non-woven fabric in the same way as in Example 4. The non-woven fabric had a weight of 540 g/m.sup.2 and a thickness of 2.8 mm. Columnar streams of water that were pressurized to 70 kg/cm.sup.2 were jetted to one surface of the non-woven fabric while it was being moved, using the same nozzle as used in Example 4 and this treatment was carried out five times at the same conditions and twice while the pressure was reduced to 30 kg/cm.sup.2. The non-woven fabric was dipped into hot water at 95.degree. C. for the shrinkage treatment and was squeezed by a mangle. The thickness of the resulting entangled non-woven sheet was reduced to about 1.8 mm and the layer of about 1/2 of the total thickness from the water jet stream treatment surface had a **fiber** structure in which ultrafine **fibers** of an average size of about 0.15 denier were branched and the fine bundles of ultrafine **fibers** were very densely entangled with one another, and the surface of the non-woven fabric had extremely little unevenness.

Detailed Description Text - DETX (79):

Using the same impregnation solution comprising a 10% polyurethane solution as used in Example 4, the procedures of impregnation, coagulation, washing with water and drying were carried out in the same way as in Example 4. Next, polystyrene and polyethylene glycol were dissolved and removed using trichloroethylene. After the non-woven fabric was sliced to a thickness of 1.1 mm, a coating prepared by adding carbon black and dyes to the polyurethane solution was applied to the surface layer which was subjected to the water jet stream treatment, using a gravure coater. After the sheet was dried and pressed for integration to produce a composite structure, grain patterning of the composite structure was effected. The opposite surface was buffed to fluff the ultrafine **fibers**. Next using disperse dyes, the sheet was dyed at a temperature of 120.degree. C. and was then finished in a customary manner. The resulting grained sheet had less repulsive feel but had integral hand characteristics such as flexibility and suppleness, had fluff of relatively long ultrafine **fibers** on one surface and a grained surface of high quality appearance on the other surface.

Detailed Description Text - DETX (81):
After the polyurethane and finishing agent were removed from the grain of the grained sheet, the average distance between the **fiber** entangling points was measured. It was found to be 98 microns.

Detailed Description Text - DETX (83):
Specific islands-in-a-sea type **fibers** consisting of polyethylene terephthalate as the island component and a mixture of polystyrene and polyethylene glycol (molecular weight 20,000) as the sea component (island/sea weight ratio=60/40) and having cross section in which 16 island-in-a-sea type structures, in each of which 8 islands were present in a sea component, were encompassed by one sea component of polystyrene, were spun using an islands-in-a-sea type **fiber** spinning die disclosed in Japanese Patent Laid-Open No. 125718/1979. The island/total sea ratio of the **fibers** was 48/52. The yarns thus obtained were stretched to 2.5 times the original length, **crimped** and cut to provide 3.8 denier, 51 mm long staple **fibers**. Each island component was an ultrafine **fiber** of 0.014 denier. The staple **fibers** were then passed through the steps of opening, carding, cross lapping and needle punching to provide a non-woven fabric. Columnar streams of water pressurized to 150 kg/cm.sup.2 were jetted to one surface of the non-woven fabric while it was being moved, from a jet nozzle having apertures having a 0.1 mm diameter and arranged in a line with 0.6 mm gaps there between with oscillating of the nozzle. This treatment was repeated three times and the non-woven fabric was then dried.

Detailed Description Text - DETX (85):

Thereafter, the sheet was treated with trichloroethylene to remove the sea component of the multi-component **fibers**. Then, the back of the sheet was buffed by 150 mesh sand paper to fluff the surface and a polyurethane type finishing agent containing a pigment was applied to the grain in a quantity of 2 g/m.sup.2 using a gravure coater and was then dyed at 120.degree. C. for one hour using a high temperature dyeing machine while crumpling the sheet. The resulting sheet had grain on one surface and fluff on the other.

Detailed Description Text - DETX (86):

The non-woven fabric, after the treatment with the water jet streams, was examined by a scanning electron microscope, and the surface was found to have a **fiber** structure in which the fibrillated ultrafine **fibers** and the bundles were entangled with one another. The distance between the **fiber** entangling points was found to be 85 microns. The portion below the surface was found to have a structure in which a large number of ultrafine **fibers were bundled** to form primary **fiber** bundles and the layer further below the former was found to have a **fiber** structure in which a plurality of the primary **fiber** bundles described above were further gathered to form an entangled layer consisting principally of secondary **fiber** bundles. One of the surfaces of the finished sheet had a grain which was composed of the fibrillated **fibers** and the resin encompassing the fibrillated **fibers** and was integrated therewith by embossing. It was further observed that the layer of the primary **fiber** bundles and the porous structure a polyurethane were present below the grain, and the layer of the secondary **fiber** bundles and the porous structure of polyurethane further continued below the former down to the back of the sheet. The other surface of the sheet was suede-like surface having dense and beautiful fluff and the fluff was seen continuing from the secondary **fiber** bundles.

Detailed Description Text - DETX (89):

4.0 denier, 51 mm long staple **fibers** of specific islands-in-a-sea type **fibers** having a composition consisting of 60 parts of a vinyl type polymer obtained by copolymerizing 20 parts of 2-ethylhexylacrylate and 80 parts of styrene as the binding component (sea component), and 40 parts of nylon 6 as the extra-ultrafine **fiber** component (islands component) and containing 16 island component groups in one filament with each island component groups containing further a large number of the extra-ultrafine **fibers** were passed through a card and a cross lapper to form a web. The average size of the extra-ultrafine **fibers** was about 0.0003 denier. The web was then needle-punched using needles, each having one hook, so as to entangle the specific island-in-a-sea type **fibers** with one another and to produce a non-woven fabric. The resulting non-woven fabric had a weight of about 450

g/m.sup.2 and an apparent density of 0.18 g/cm.sup.3.

Detailed Description Text - DETX (91):

Thereafter, the sheet was repeatedly dipped into trichloroethylene and squeezed to extract and substantially completely remove the vinyl type polymer sea component of the **fiber**. The sheet was then dried and was dyed with metal-complex dye using a normal-pressure winch dyeing machine. After a softening agent was applied, the sheet was crumpled and finished.

Detailed Description Text - DETX (92):

The resulting leather-like sheet had a weight of 220 g/m.sup.2, an apparent density of 0.36 g/cm.sup.3, a clear grain pattern and excellent flexibility. When the sheet was strongly crumpled by hand, neither scratching nor damage occurred and the sheet was found to have high flexibility resistance as well as high scratch and scuff resistance. After polyurethane was removed from the grain of the grained sheet, the average distance between the **fiber** entangling points of the constituent **fibers** was measured. It was found to be 23 microns.

Detailed Description Text - DETX (94):

3.8 denier, 38 mm long staple **fibers** of mixed spun **fibers** obtained by mixing and spinning two components, which have a composition consisting of 45 parts of polystyrene as the binding component, and 55 parts of nylon 6 as the ultrafine **fiber** component, were passed through a random webber to form a web. The average size of the ultrafine **fibers** was about 0.002 denier. The web was then needle-punched using needles, each having three hooks, so as to entangle the mixed spun **fibers** with one another and to produce a non-woven fabric. The resulting non-woven fabric had a weight of about 350 g/m.sup.2 and an apparent density of 0.19 g/cm.sup.3.

Detailed Description Text - DETX (97):

The resulting sheet had a weight of 240 g/m.sup.2, an apparent density of 0.32 g/cm.sup.3, and showed excellent appearance, high softness, and excellent hand characteristics. This sheet developed neither cracking nor fluffing even when the sheet was strongly rubbed or pulled by hand. After polyurethane was removed from the grain of the grained sheet, the average distance between the **fiber** entangling points of the constituent **fibers** was measured to be 46 microns.

Detailed Description Text - DETX (99):

2.4 denier, 38 mm long staple **fibers** of multi-layered **bicomponent** type **fibers** having a doughnut-like (as shown in FIG. ~~4(e)) cross-section~~, which have a composition consisting of 50 parts of polyethylene terephthalate and 50 parts

of nylon 66 and have 30 segments, were passed through a random webber to form a web. The average size of each segment was about 0.08 denier. The web was then needle-punched so as to entangle the multi-layered **bicomponent** type **fibers** with one another. The resulting needle-punched sheet had a weight of about 460 g/m.sup.2 and an apparent density of 0.17 g/cm.sup.3.

Detailed Description Text - DETX (107):
The non-woven fabric, after the treatment with the water jet streams, was examined by a scanning electron microscope, and the surface was found to have a **fiber** structure in which the fibrillated ultrafine **fibers** and the bundles were entangled with one another. The distance between the **fiber** entangling points was found to be 124 microns.

Detailed Description Text - DETX (109):
Islands-in-a-sea type **fibers** of 3.8 denier, having a composition consisting of 50 parts of polyethylene terephthalate as the ultrafine **fiber** component (islands component) and 50 parts of the binding component (sea component) consisting of 45 parts of polystyrene and 5 parts of polyethyleneetherglycol of a molecular weight 20,000, and containing 16 ultrafine **fibers** in one filament, were **crimped** and cut to a length of about 51 mm, and were thereafter passed through a card and a cross lapper to obtain a web. The web was needle-punched to obtain a non-woven fibrous sheet having a thickness of about 1.0 mm and a weight of about 190 g/m.sup.2. The non-woven web was then needle-punched to form a non-woven fibrous sheet having a thickness of about 3.0 mm and a weight of about 540 g/m.sup.2.

Detailed Description Text - DETX (111):
The resulting non-woven fibrous sheet was examined by a scanning electron microscope, and it was found that the fibrillated ultrafine **fibers** were entangled with one another, especially near the surfaces. The non-woven fibrous sheet also had good suppleness and excellent shape retention without dissolving the binding component.

Detailed Description Text - DETX (113):
4.0 denier, 51 mm long staple **fibers** of mixed spun **fibers** obtained by mixing and spinning two components which have a composition consisting of 50 parts of nylon 6 as the ultra **fiber** component, and 50 parts of the binding component comprising 40 parts of copolymer of 2-ethylhexyl acrylate/styrene (20/80) and 10 parts of polyethyleneetherglycol of a molecular weight 50,000 were passed through an opener, a card and a cross lapper to form a web. The web was needle-punched to obtain a needle-punched sheet having a thickness of about 3.0 mm and a weight of about 540 g/m.sup.2.

Detailed Description Text - DETX (115):

The jetted sheet was examined by a scanning electron microscope, and it was found that most of the binding components were removed, and the resulting ultrafine **fiber** bundles consisting of ultrafine **fiber** of about 0.009 denier were highly fibrillated and the fibrillated ultrafine **fibers** were densely entangled with one another, especially near the surfaces. The jetted sheet was then impregnated with a 10% emulsion of polyurethane and was dried. Thereafter the sheet was dipped in perchloroethylene and dried. The remaining binding component was easily removed. A leather-like grain pattern was applied to one surface of the dried sheet using a hot embossing roller. The sheet was then dyed red. The dyed sheet showed an extremely dense and smooth surface like that of natural grain leather. Moreover, it had excellent supple touch and flexibility.

Claims Text - CLTX (1):

1. An entangled nonwoven fabric comprising a portion (A) and a portion (B), said portion (A) being comprised of ultrafine **fiber** bundles, the ultrafine **fibers** of said bundles having a size not greater than about 0.5 denier, said **fiber** bundles of said portion (A) being entangled with one another; and said portion (B) comprising either ultrafine **fibers** or fine bundles of ultrafine **fibers** or both, each branching from said ultrafine **fiber** bundles (A), said fine bundles of portion (B) having a size less than said bundles of portion (A);

Claims Text - CLTX (2):

the ultrafine **fibers** of said portion (B) being entangled with one another;

Claims Text - CLTX (5):

3. The entangled non-woven fabric as defined in claim 1, wherein said ultrafine **fibers** forming said portions (A) and (B) are substantially continuous through portions (A) and (B).

Claims Text - CLTX (6):

4. The entangled non-woven fabric as defined in claim 1 wherein said ultrafine **fibers** are formed from composite **fibers** selected from the group consisting of multilayered **bicomponent** type **fibers,** chrysanthemum-like cross-section **bicomponent fibers,** mixed spun multi-component **fibers** and islands-in-a-sea type **fibers**.

Claims Text - CLTX (7):

5. The entangled non-woven fabric as defined in claim 1 wherein said ultrafine **fibers** are comprised of a polymer material selected from the group

consisting of nylon 6, nylon 66, nylon 12, copolymerized nylon, polyethylene terephthalate, polybutylene terephthalate, copolymerized polyethylene terephthalate, copolymerized polybutylene terephthalate, polyethylene, polypropylene, polyurethane, polyacrylonitrile, vinyl polymers and combinations thereof.

Claims Text - CLTX (8):

6. A grained sheet having on at least one of its surfaces a grain formed by a composite structure comprising a **fiber** structure composed of ultrafine **fibers** or fine bundles of said ultrafine **fibers** or both and having a distance between the **fiber** entangling points of not greater than about 200 microns, and a resin in the gap portions of said **fiber** structure.

Claims Text - CLTX (9):

7. The grained sheet as defined in claim 6 wherein the lower layer of said grain comprises ultrafine **fibers** bundles that are entangled with one another, said grain comprises ultrafine **fibers** to fine bundles of ultrafine **fibers** branching from said ultrafine **fiber** bundles of said lower layer, said **fibers** in said lower layer and in said grain are substantially continuous and the degree of branching of said **fibers** changes continuously around the boundary portion between said layers.

Claims Text - CLTX (10):

8. The grain sheet as defined in claim 6 wherein the distance between said **fiber** entangling points is not greater than about 100 microns.

Claims Text - CLTX (11):

9. The grained sheet as defined in claim 6 wherein said ultrafine **fibers** are not greater than about 0.2 denier.

Claims Text - CLTX (12):

10. The grained sheet as defined in claim 6 wherein said ultrafine **fibers** are not greater than about 0.05 denier.

Claims Text - CLTX (13):

11. The grained sheet as defined in claim 6 wherein said ultrafine **fibers** are formed from composite **fibers** selected from the group consisting of multilayered **bicomponent** type **fibers,** chrysanthemum-like cross-section **bicomponent fibers,** mixed spun multicomponent **fibers** and islands-in-a-sea type **fibers**.

Claims Text - CLTX (14):

12. The grained sheet as defined in claim 6 wherein said ultrafine **fibers** are comprised of a polymer material selected from the group consisting of nylon 6, nylon 66, nylon 12, copolymerized nylon, polyethylene terephthalate, polybutylene terephthalate, copolymerized polyethylene terephthalate, copolymerized polybutylene terephthalate, polyethylene, polypropylene, polyurethane, polyacrylonitrile, vinyl polymers and combinations thereof.

Claims Text - CLTX (16):
14. The grained sheet as defined in claim 13 wherein said resin is selected from the group consisting of **polyamide,** polyester, polyvinyl chloride, polyacrylate copolymers, polyurethane, neoprene, styrene/butadiene copolymers, acrylonitrile/butadiene copolymers, polyamino acids, polyamino acid/polyurethane copolymers, silicone resins and mixtures thereof.

Claims Text - CLTX (18):
16. A method of producing an entangled non-woven fabric including a portion (A) comprised of ultrafine **fiber** bundles entangled with one another and a portion (B), said portion (B) comprising either ultrafine **fibers** of fine bundles of ultrafine **fibers** or both, branching from said ultrafine **fiber** bundles and entangled with one another; said method comprising the steps of:

Claims Text - CLTX (19):
(1) forming a **fiber** entangled sheet by use of **fibers** comprising an ultrafine **fiber** component and a bonding component which bonds said ultrafine **fiber** components, arranged in the longitudinal direction of the **fibers** in an arbitrary cross-section, said components being polymer materials having a different solvent solubility from each other;

Claims Text - CLTX (20):
(2) dissolving and removing said binding component by use of a solvent which can dissolve said binding component but not said **fiber** components, and

Claims Text - CLTX (21):
(3) applying a high speed fluid jet stream to said **fibers** so as to branch and entangle said **fibers** and to produce a degree of branching continuously along the boundary portion between both portions (A) and (B).

Claims Text - CLTX (25):
20. A method of producing an entangled non-woven fabric including a portion (A) comprised of ultrafine **fiber** bundles entangled with one another and a portion (B) comprised of ultrafine **fibers** or fine bundles of ultrafine **fiber** bundles or both, and entangled with one another, said method comprising the

steps of:

Claims Text - CLTX (26):
(1) forming a **fiber** sheet by use of **fibers** comprising an ultrafine **fiber** component and a bonding component which bonds said ultrafine **fiber** component, arranged in the longitudinal direction of the **fibers** in an arbitrary cross-section, said components being polymer materials having a different solvent solubility from each other;

Claims Text - CLTX (27):
(2) applying high speed fluid jet streams so as to branch and entangle said branched **fibers**; and

Claims Text - CLTX (28):
(3) dissolving and removing said binding component by use of a solvent which can dissolve said binding components but cannot dissolve said **fibers,** thus producing a degree of branching changing continuously along the boundary portion between both portions (A) and (B).

Claims Text - CLTX (29):
21. The method of producing an entangled non-woven fabric as defined in claim 16, further comprising the step of needle-punching said **fiber** entangled sheet prior to said dissolving and removing step (2).

Claims Text - CLTX (30):
22. The method of producing an entangled non-woven fabric as defined in claim 16 further including the steps of applying a resin to temporarily fix said **fiber** entangled sheet prior to said dissolving and removing step (2) and then removing said resin after dissolving and removing said binding component.

Claims Text - CLTX (32):
24. A method of producing a grained sheet having on at least one of its surfaces a grain formed by a **fiber** structure composed of ultrafine **fibers** or fine bundles of said ultrafine **fibers** or both and having a distance between the **fiber** entangling points of not greater than about 200 microns, and a resin present in the gap portions of said **fiber** structure, said method comprising the steps of:

Claims Text - CLTX (33):
(1) forming a **fiber** sheet using **fibers** selected from ultrafine **fiber** formable **fibers** and ultrafine **fibers**;

Claims Text - CLTX (34):
(2) applying a high speed fluid jet stream to said **fiber** sheet to branch and entangle said **fibers**;

Claims Text - CLTX (37):
25. The method of producing a grained sheet as defined in claim 24 wherein said ultrafine **fiber** formable **fibers** are those which have a cross-section in which a plurality of cores are at least partially bonded by other components.

Claims Text - CLTX (38):
26. The method of producing a grained sheet as defined in claim 24 wherein said ultrafine **fiber** formable **fibers** are multiple-component **fibers which provide fiber** bundles of ultrafine **fibers** not greater than 0.2 denier when at least one of their components is dissolved and removed.

Claims Text - CLTX (39):
27. The method of producing a grained sheet as defined in claim 26 wherein said ultrafine **fibers** are not greater than 0.05 denier.

Claims Text - CLTX (40):
28. The method of producing a grained sheet as defined in claim 24 wherein said ultrafine **fiber** formable **fibers are those which have a fiber** structure in which a plurality of extra-ultrafine **fibers** are aggregated and bonded together by other components to form one ultrafine **fiber** and a plurality of said ultrafine **fibers** are aggregated and bonded by other components to form one **fiber**.

Claims Text - CLTX (41):
29. The method of producing a grained sheet having on at least one of its surfaces a grain formed by a **fiber** structure composed of ultrafine **fibers** to fine bundles of said ultrafine **fibers** and having a distance between the **fiber** entangling points of not greater than about 200 microns, and resin present in the gap portions of said **fiber** structure, as defined in claims 24, 25, 26, 27 or 28 wherein a step of dissolving and removing part of the components of said ultrafine **fiber** formable **fibers** by use of a solvent capable of dissolving said part of the components so as to modify said ultrafine **fiber** formable **fibers** into a plurality of ultrafine **fibers** is inserted into the production process of said sheet at a suitable step.

Claims Text - CLTX (42):
30. A method of producing a grained sheet having on at least one of its surfaces a grain formed by a **fiber** structure composed of ultrafine **fibers** or

fine bundles of said ultrafine **fibers** or both, said **fibers** being tangled at **fiber** entangling points, and having a distance between the **fiber** entangling points of not greater than about 200 microns, and said sheet having an applied resin present in the gap portions of said **fiber** structure, wherein said entangled non-woven fabric as defined in claim 1, 2, or 3 is used as the starting material and resin is applied to at least said portion (B) of said non-woven fabric to form the grain.

Claims Text - CLTX (43):

31. The method of producing a grained sheet as defined in claim 29 wherein said part of components of said ultrafine **fiber** formable **fibers** contains a heterogeneous substance.

Claims Text - CLTX (46):

34. The method of providing a grained sheet as defined in claim 24, further comprising the step of heat-pressing said entangled **fiber** sheet before applying resin.